



DEPARTMENT OF THE NAVY  
NAVAL RESEARCH LABORATORY  
4555 OVERLOOK AVE SW  
WASHINGTON D C 20375-5320

IN REPLY REFER TO:

Navy Case No. 79,702

## APPLICATION FOR LETTERS PATENT

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT Douglas B. Chrisey, R. Andrew McGill, and Alberto Pique are citizens of the United States of America, and residents of Bowie, MD, Lorton, VA, and Bowie, MD have invented certain new and useful improvements in "MATRIX ASSISTED PULSED LASER EVAPORATION DIRECT WRITE" of which the following is a specification:

Prepared by:  
Ralph T. Webb  
Reg. No. 33047  
Tele. No. (202) 404-1554

000000-99112560

## MATRIX ASSISTED PULSED LASER EVAPORATION DIRECT WRITE

Insa!**Background of the Invention****1. Field of the Invention**

The invention relates generally to the deposition of materials and more specifically to devices, materials and methods for direct writing of a wide range of different materials onto substrates.

**2. Description of the Related Art**

The term "direct write" refers generally to any technique for creating a pattern directly on a substrate, either by adding or removing material from the substrate, without the use of a mask or preexisting form. Direct write technologies have been developed in response to a need in the electronics industry for a means to rapidly prototype passive circuit elements on various substrates, especially in the mesoscopic regime, that is, electronic devices that straddle the size range between conventional microelectronics (sub-micron-range) and traditional surface mount components (10+ mm-range). (Direct writing may also be accomplished in the sub-micron range using electron beams or focused ion beams, but these techniques, because of their small scale, are not appropriate for large scale rapid prototyping.) Direct writing allows for circuits to be prototyped without iterations in photolithographic mask design and allows the rapid evaluation of the performance of circuits too

1 difficult to accurately model. Further, direct writing allows for the size of printed circuit boards and  
2 other structures to be reduced by allowing passive circuit elements to be conformably incorporated  
3 into the structure. Direct writing can be controlled with CAD/CAM programs, thereby allowing  
4 electronic circuits to be fabricated by machinery operated by unskilled personnel or allowing  
5 designers to move quickly from a design to a working prototype. Mesoscopic direct write  
6 technologies have the potential to enable new capabilities to produce next generation applications  
7 in the mesoscopic regime. Other applications of direct write technologies in microelectronic  
8 fabrication include forming ohmic contacts, forming interconnects for circuit and photolithographic  
9 mask repair, device restructuring and customization, design and fault correction.

10 Currently known direct write technologies for adding materials to a substrate include ink jet  
11 printing, Micropen<sup>®</sup>, laser chemical vapor deposition (LCVD) and laser engineered nano-shaping  
12 (LENS). Currently known direct write technologies for removing material from a substrate include  
13 laser machining, laser trimming and laser drilling.

14 The direct writing techniques of ink jet printing, screening and Micropen<sup>®</sup> are wet  
15 techniques, that is, the material to be deposited is combined with a solvent or binder and is squirted  
16 onto a substrate. The solvent or binder must later be removed by a drying or curing process, which  
17 limits the flexibility and capability of these approaches. In addition, wet techniques are inherently  
18 limited by viscoelastic properties of the fluid in which the particles are suspended or dissolved.

19 In the direct writing technique known as "laser induced forward transfer" (LIFT), a pulsed  
20 laser beam is directed through a laser-transparent target substrate to strike a film of material coated

1 on the opposite side of the target substrate. The laser vaporizes the film material as it absorbs the  
2 laser radiation and, due to the transfer of momentum, the material is removed from the target  
3 substrate and is redeposited on a receiving substrate that is placed in proximity to the target  
4 substrate. Laser induced forward transfer is typically used to transfer opaque thin films, typically  
5 metals, from a pre-coated laser transparent support, typically glass,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SrTiO}_3$ , etc., to the  
6 receiving substrate. Various methods of laser-induced forward transfer are described in, for example,  
7 the following U.S. patents and publications incorporated herein by reference: U.S. Patent No.  
8 4,752,455 to Mayer, U.S. Patent No. 4,895,735 to Cook, U.S. Patent No. 5,725,706 to Thoma et al,  
9 U.S. Patent No. 5,292,559 to Joyce, Jr. et al, U.S. Patent No. 5,492,861 to Opower, U.S. Patent No.  
10 5,725,914 to Opower, U.S. Patent No. 5,736,464 to Opower, U.S. Patent No. 4,970,196 to Kim et  
11 al, U.S. Patent No. 5,173,441 to Yu et al, and Bohandy et al, "Metal Deposition from a Supported  
12 Metal Film Using an Excimer Laser, J. Appl. Phys. 60 (4) 15 August 1986, pp 1538 - 1539. Because  
13 the film material is vaporized by the action of the laser, laser induced forward transfer is inherently  
14 a homogeneous, pyrolytic technique and typically cannot be used to deposit complex crystalline,  
15 multi-component materials or materials that have a crystallization temperature well above room  
16 temperature because the resulting deposited material will be a weakly adherent amorphous coating.  
17 Moreover, because the material to be transferred is vaporized, it becomes more reactive and can  
18 more easily become degraded, oxidized or contaminated. The method is not well suited for the  
19 transfer of organic materials, since many organic materials are fragile and thermally labile and can  
20 be irreversibly damaged during deposition. Moreover, functional groups on an organic polymer can

1 be irreversibly damaged by direct exposure to laser energy. Other disadvantages of the laser induced  
2 forward transfer technique include poor uniformity, morphology, adhesion, and resolution. Further,  
3 because of the high temperatures involved in the process, there is a danger of ablation or sputtering  
4 of the support, which can cause the incorporation of impurities in the material that is deposited on  
5 the receiving substrate. Another disadvantage of laser induced forward transfer is that it typically  
6 requires that the coating of the material to be transferred be a thin coating, generally less than 1  $\mu\text{m}$   
7 thick. Because of this requirement, it is very time-consuming to transfer more than very small  
8 amounts of material.

9 In a simple variation of the laser induced forward deposition technique, the target substrate  
10 is coated with several layers of materials. The outermost layer, that is, the layer closest to the  
11 receiving substrate, consists of the material to be deposited and the innermost layer consists of a  
12 material that absorbs laser energy and becomes vaporized, causing the outermost layer to be  
13 propelled against the receiving substrate. Variations of this technique are described in, for example,  
14 the following U.S. patents and publications incorporated herein by reference: U.S. Patent No.  
15 5,171,650 to Ellis et al, U.S. Patent No. 5,256,506 to Ellis et al, U.S. Patent No. 4,987,006 to  
16 Williams et al, U.S. Patent No. 5,156,938 to Foley et al and Tolbert et al, "Laser Ablation Transfer  
17 Imaging Using Picosecond Optical pulses: Ultra-High Speed, Lower Threshold and High  
18 Resolution" Journal of Imaging Science and Technology, Vol. 37, No. 5, Sept./Oct. 1993pp.485-489.  
19 A disadvantage of this method is that, because of the multiple layers, it is difficult or impossible to  
20 achieve the high degree of homogeneity of deposited material on the receiving substrate required,

1 for example, for the construction of electronic devices, sensing devices or passivation coatings.

2 Therefore, there is a strong need for devices and methods for transferring materials for uses  
3 such as in electronic devices, sensing devices or passivation coatings with in such a way that desired  
4 properties of the materials are preserved or enhanced. For example, there is a need for a method to  
5 transfer powders or particulate materials so that they retain their bulk properties. With respect to  
6 novel materials such as organic polymers that are incorporated into electronic devices, there is a need  
7 for a method to transfer these materials in such a way that their structural and chemical integrity is  
8 retained.

#### 9 10 **Summary of the Invention**

11 It is an object of the present invention to provide devices, materials and methods for  
12 depositing a material on a substrate wherein a pattern can be created directly on the substrate without  
13 the use of a mask.

14 It is an object of the present invention to provide a device and method that is useful for  
15 depositing a wide range of materials such as complex polymeric materials or complex electronic  
16 materials, with no damage to the starting material.

17 It is a further object of the present invention to provide a device and method for depositing  
18 a material on a substrate wherein the deposition can be carried out in ambient conditions, that is, at  
19 atmospheric pressure and at room temperature.

20 It is a further object of the present invention to provide a device ad method for depositing a

1 material on a substrate by laser induced deposition wherein the spatial resolution of the deposited  
2 material can be as small as 1  $\mu\text{m}$ .

3 It is an object of the present invention to provide equipment and a method for creating an  
4 electronic device, sensor, or passivation coating by depositing a materials on a substrate in a  
5 controlled manner wherein the process can be computer-controlled.

6 It is an object of the present invention to provide equipment and a method for creating an  
7 electronic device, sensor or passivation coating by depositing a materials on a substrate in a  
8 controlled manner wherein it is possible to switch rapidly between different materials to be deposited  
9 on the substrate.

10 These and other objects are achieved by a device and method for depositing a material onto  
11 a receiving substrate, the device comprising a source of pulsed laser energy, a receiving substrate,  
12 and a target substrate. The target substrate comprises a laser transparent support having a back  
13 surface and a front surface. The front surface has a coating that comprises a mixture of the transfer  
14 material to be deposited and a matrix material. The matrix material has the property that, when it is  
15 exposed to pulsed laser energy, it is more volatile than the transfer material. The source of pulsed  
16 laser energy can be positioned in relation to the target substrate so that pulsed laser energy can be  
17 directed through the back surface of the target substrate and through the laser-transparent support  
18 to strike the coating at a defined location with sufficient energy to volatilize the matrix material at  
19 the location, causing the coating to desorb from the location and be lifted from the surface of the  
20 support. The receiving substrate can be positioned in a spaced relation to the target substrate so that

1 the transfer material in the desorbed coating can be deposited at a defined location on the receiving  
2 substrate and so that the matrix material, or decomposition products thereof, in the desorbed coating  
3 can migrate from the space between the receiving substrate and the target substrate.

4 The source of pulsed laser energy and the target substrate can be moved with respect to each  
5 other so that after the coating desorbs at one location on the target substrate, the pulsed laser energy  
6 can be directed to another location on the target substrate where the coating has not yet desorbed.  
7 The source of pulsed laser energy and the receiving substrate can be moved with respect to each  
8 other so that the transfer material can be deposited in a pattern. The source of pulsed laser energy  
9 can also be directed through a transparent region of the target substrate, or the target substrate can  
10 be moved completely out of the way so that the pulsed laser energy strikes the receiving substrate  
11 directly and interacts with the receiving substrate or with material already deposited on the receiving  
12 substrate. This can be done, for example, to roughen the surface of the receiving substrate or to  
13 modify the composition and properties of material that has been deposited.  
14

#### 15 **Brief Description of the Drawings**

16 A more complete appreciation of the invention will be readily obtained by reference to the  
17 following Description of the preferred Embodiments and the accompanying drawings.

18 Figure 1 is a schematic representation of the apparatus of the present invention.

19 Figures 2a and 2b are schematic representations of the laser transparent substrate, the coating  
20 and the receiving substrate before (2a) and after (2b) the depositing of the transfer material on the



1 receiving substrate.

## 2 Detailed Description of the Preferred Embodiments

3 As schematically illustrated in Figure 1, the apparatus of the present invention includes a  
4 pulsed laser 12 that emits pulsed laser energy as depicted by arrow 14. The pulsed laser is positioned  
5 so that laser pulses travel through the back surface of the target substrate and through the laser  
6 transparent support 15 to strike the coating 16, which comprises a mixture of a transfer material and  
7 a matrix material. The receiving substrate 18 is positioned so that when the coating desorbs from the  
8 target substrate, the transfer material is deposited on the receiving substrate. The laser, the target  
9 substrate and the receiving substrate are connected to laser positioning means 20, target substrate  
10 positioning means 22 and receiving substrate positioning means 24, respectively. Figures 2a and 2b  
11 schematically illustrate the effects of exposing the coating 16 to the pulsed laser energy 14, whereby  
12 the coating 16 desorbs from the surface of the target substrate so that the transfer material 26 is  
13 deposited onto the receiving substrate 18.

14 The receiving substrate can be any material, planar or non-planar onto which one may wish  
15 to deposit a transfer material. The receiving substrate may be any solid material including, but not  
16 limited to, silicon, glass, plastics, metals, and ceramics. The present invention is particularly useful  
17 in creating electronic devices such as passive and active components of printed circuit boards (PCBs)  
18 or in creating chemoselective coatings for chemical sensors such as surface acoustic wave (SAW)  
19 resonators.

20 The transfer material can be any material that one may wish to deposit on a substrate in a

1 defined pattern, including, but not limited to the following:

2 Metals, including, but not limited to silver, nickel, gold, copper, chromium, titanium,  
3 aluminum, platinum, palladium, etc., and alloys thereof;

4 Ceramics, including, but not limited to alumina ( $\text{Al}_2\text{O}_3$ ), silica and other glasses, and  
5 dielectrics (see below);

6 Dielectrics, including, but not limited to alumina, magnesium oxide ( $\text{MgO}$ ), yttrium  
7 oxide ( $\text{Y}_2\text{O}_3$ ), zirconium oxide ( $\text{ZrO}_2$ ), cerium oxide ( $\text{CeO}_2$ ), etc.;

8 Ferroelectrics, including, but not limited to barium titanate ( $\text{BaTiO}_3$ ), strontium titanate  
9 ( $\text{SrTiO}_3$ ), lead titanate ( $\text{PbTiO}_3$ ), lead zirconate ( $\text{PbZrO}_3$ ), potassium niobate ( $\text{KNbO}_3$ ), strontium  
10 bismuth tantalate ( $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ), ( $\text{Ba,SrTiO}_3$ ), and solid solution stoichiometric variations thereof,  
11 etc. ;

12 Piezoelectrics, including, but not limited to the above mentioned ferroelectrics, quartz,  $\text{AlN}$ ,  
13 etc.;

14 Ferrites, including but not limited to yttrium iron garnet ( $\text{Y}_3\text{Fe}_5\text{O}_{12}$ ), barium zinc ferrite  
15 ( $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{19}$ ), hexagonal ferrites such as barium ferrite, spinel ferrites such as nickel zinc ferrites,  
16 manganese zinc ferrite, magnetite ( $\text{Fe}_3\text{O}_4$ ), etc.;

17 Electro-optical ceramics, including, but not limited to lithium niobate ( $\text{LiNbO}_3$ ), lithium  
18 tantalate ( $\text{LiTaO}_3$ ), cadmium telluride ( $\text{CdTe}$ ), zinc sulfide ( $\text{ZnS}$ ), etc.;

19 Ceramic superconductors, including, but not limited to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO),  
20  $\text{Tl}_2\text{CaBa}_2\text{Cu}_3\text{O}_{12}$ ,  $\text{La}_{1.4}\text{Sr}_{0.6}\text{CuO}_{3.1}$ ,  $\text{BiSrCACuO}$ ,  $\text{BaKBiO}$ , halide doped fullerenes, etc.;

Inventor's Name: Douglas B. Chrisey, R. Andrew McGill and Alberto Pique

1 Chalcogenides, including, but not limited to SrS, ZnS, CaS, PbS, etc.;

2 Chemoselective materials (see below);

3 Bioselective materials (see below);

4 Semiconductors, including, but not limited to Si, Ge, GaAs, CdTe, etc.;

5 Phosphors, including, but not limited to SrS:Eu, SrS:Ce, ZnS:Ag, Y<sub>2</sub>O<sub>3</sub>:Eu, Zn<sub>2</sub>SiO<sub>4</sub>:Mn,

6 etc.and

7 Transparent conductive oxides, including, but not limited to indium tin oxide, zinc oxide, etc.

8 For example, if the receiving substrate is a component of an electronic device, the transfer

9 material can be a material having particular desired electronic properties. Examples of electronic

10 materials include metals, dielectrics, ferroelectrics, ferrites, ferrimagnets, ferromagnets,

11 semiconductors, phosphors and electrically conducting organic polymers.

12 If the receiving substrate is a component of a chemical or biological sensor, the transfer

13 material can be a material that interacts selectively with a particular chemical or biological analyte.

14 Criteria for selecting chemically selective materials for chemical sensing devices are described in

15 detail in McGill et al, "Choosing Polymer Coatings for Chemical Sensors", CHEMTECH, Vol 24,

16 No. 9, pp 27-37 (1994), the disclosure of which is incorporated herein by reference. Examples of

17 chemoselective materials include SXFA (poly(oxy{methyl[4-hydroxy-4,4,bis(trifluoromethyl)but-1-

18 en-1-yl]silylene})), P4V (poly(4-vinylhexafluorocumyl alcohol). Other examples of chemoselective

19 materials include perfluoro-polyethers terminated with a variety of functional groups such as

20 CF<sub>3</sub>CH<sub>2</sub>OH, polyethylene imines, polysiloxanes, alkylamino pyridyl substituted polysiloxanes,

1 polytetrafluoroethylene, polysilanes, polyesters, polyvinylaldehydes, polyisobutylene,  
2 polyvinylesters, polyalkenes, zeolites, aerogels, porous carbon, metals, silicalites, clay materials,  
3 cellulose materials, polyanilines, polythiophenes, polypyrroles, fullerenes, cyclodextrins,  
4 cyclophanes, calixeranes, crown ethers, and organic dyes.

5 Examples of biochemical materials that can be deposited with the present invention include  
6 proteins, oligopeptides, polypeptides, whole cells, biological tissue, enzymes, cofactors, nucleic  
7 acids, DNA, RNA, antibodies (intact primary, polyclonal, and monoclonal), antigens,  
8 oligosaccharides, polysaccharides, oligonucleotides, lectins, biotin, streptavidin, and lipids.

9 The receiving substrate may be a component of a physical sensing device, such as, for  
10 example, a magnetic sensor, optical sensor, temperature sensor, pressure sensor or gas flow sensor.  
11 The transfer material may then be an appropriate sensing material, such as a magnetic sensing  
12 material, optical sensing material, temperature sensing material, pressure sensing material or gas  
13 flow sensing material. Examples of physical sensing transfer materials include magnetic-  
14 nonmagnetic multilayers or resonant magnetic oscillators for magnetic sensing, thin film  
15 thermocouples for temperature sensing, piezoelectric films or resonators for pressure sensing and  
16 simple resistive heater-thermocouple combinations for gas flow sensing.

17 In many instances, the desired properties of a material are due to the presence of functional  
18 groups in the material. For example chemoselective polymers such as SXFA and P4V derive their  
19 chemoselectivity from functional groups that extend outward from the polymer backbone. A purpose  
20 of the present invention is to provide a way to deposit these polymers onto a substrate without

1     damaging or disrupting the functional groups. As another example, some materials have different  
2     electronic, mechanical and thermal properties depending on whether they are in bulk form or in the  
3     form of single crystals. For instance, a large grain size is desirable for ferroelectrics to achieve a near  
4     bulk dielectric constant and large crystalline platelets are desirable for ferrites to minimize  
5     demagnetizing forces. The transfer material in the present invention can be in any form ranging from  
6     single crystallites to nanophase powders to micron size particulates, depending on the particular  
7     intended use for the transferred material and whether bulk-like properties are desired. A purpose of  
8     the present invention is to provide a way to deposit such materials so that the desired form of the  
9     material is preserved or even improved (such as in depositing material in such a way that it is better  
10    connected or bonded than the original material). Typical particle sizes for the transfer material may  
11    range from about 10 nm to about 20  $\mu$ m. For close packing of the transfer material, the transfer  
12    material can comprise particles of different size classes, so that smaller particles can fit into  
13    interstices between larger particles. For example, for face centered cubic packing of particles, the  
14    highest packing density can be achieved by providing particles of three different sizes wherein the  
15    ratio of particle sizes is 1 : less than .414 : less than .225.

16           The transfer material may also be coated particles, such as metal or ceramic particles coated  
17    with organic materials such as organic precursors.

18           It is the presence of the matrix material that provides the advantages that the present  
19    invention has over methods such as laser induced forward transfer (LIFT). The matrix material is  
20    selected primarily according to two criteria: the matrix material must be compatible with the transfer

1 material so that the matrix material and the transfer material can be combined into a mixture to form  
2 the coating on the front surface of the laser transparent support, and the matrix material must have  
3 the property of being more volatile than the transfer material when the coating is exposed to pulsed  
4 laser energy so that when the coating is exposed to pulsed laser energy, the matrix material  
5 volatilizes or vaporizes, thereby causing the coating to desorb from the surface of the laser  
6 transparent support. The amount of matrix material that is used in the coating relative to the amount  
7 of the transfer material can be any amount sufficient to accomplish the purposes described above.  
8 Typically, the amount will vary according to the particular matrix material and transfer material.

9 Other factors that can be taken into account in selecting the optimum matrix material to go  
10 with a particular transfer material include the ability of the matrix material to dissolve or form a  
11 colloidal or particulate suspension with the particular transfer material, the melting point, heat  
12 capacity, molecular size, chemical composition, spectral absorption characteristics and heat of  
13 vaporization of the matrix material (factors that affect the ability of the matrix material to desorb and  
14 lift the transfer material from the target substrate) and the reactivity or nonreactivity of the matrix  
15 material towards the transfer material.

16 The matrix material may also serve other functions. For example, the presence of the matrix  
17 material may aid in the construction of the coating on the target substrate by helping to hold the  
18 transfer material in place on the target substrate, especially if the transfer material is a powder. At  
19 the same time, the matrix material may help prevent the transfer material from binding too tightly  
20 to the surface of the target substrate. The matrix material may also provide a source of particle

1 coating for transfer material that is in the form of a powder and provide a source of additives, binders  
2 and dispersants for the transfer material.

3 Another consideration is any special ability a particular matrix material may have to impart  
4 protection to a particular transfer material from damage during the lasing, desorption and transfer  
5 to the receiving substrate. For example, a matrix material that absorbs laser energy at the same  
6 wavelength as an important functional group on the transfer material may serve to protect the  
7 transfer material from damage from exposure to the laser energy. Alternatively, a matrix material  
8 may be used that absorbs at a wavelength in a spectral region substantially outside that of the transfer  
9 material. In this instance, the matrix material transforms pulsed laser energy into kinetic energy, and  
10 the kinetic energy is imparted to the transfer material. Examples of matrix materials include but are  
11 not limited to addition polymers (see below), condensation polymers (see below), photoresist  
12 polymers (see below), water, aryl solvents, especially toluene, acetophenone and nicotinic acid,  
13 arene compounds (e.g. naphthalene, anthracene, phenanthrene), t-butylalcohol, halogenated organic  
14 solvent, hydrocarbons, ketones, alcohols, ethers, esters, carboxylic acids, phenols and phosphoric  
15 acid.

16 The matrix material may also be a polymer that decomposes or "unzips" into volatile  
17 components when exposed to laser energy. The volatile decomposition products then act to propel  
18 or lift the transfer material into the gas phase. The polymeric matrix material acts as a propellant and  
19 at room temperature the propellant products are volatilized away while the transfer material is  
20 deposited as a thin film on the receiving substrate.

1 Unzipping mechanisms are typically catalyzed by a photon that is absorbed by the polymer  
2 and leads to chain cleavage, formation of a free radical (The free radical can be formed either by a  
3 thermally driven process or by a photochemical process) in the chain which then travels down the  
4 polymer chain leading to a chain unzipping that can produce the monomer species. The monomer,  
5 ejected at high kinetic energies, imparts some of this energy to the transfer material mixed with the  
6 polymer. One general controlling factor for depolymerization or unzipping of addition polymers is  
7 the ceiling temperature of the polymer. At the ceiling temperature, the rates of polymerization and  
8 depolymerization are equal. At temperatures above the ceiling temperature, depolymerization  
9 dominates polymerization. Laser radiation allows the high ceiling temperatures required for  
10 depolymerization to be reached between radiation pulses.

11 In general, polymeric propellants that are suitable candidates for consideration as matrix  
12 materials are taken from the class of polymers called addition polymers. As a subclass of addition  
13 polymers, the suitable candidate materials are typically sterically crowded and are generally  
14 thermally unstable. The general polymer classes that are of interest with known properties include  
15 poly(alkenes), poly(acrylics), poly(methacrylics), poly(vinyls), poly(vinylketones), poly(styrenes),  
16 poly(oxides) or polyethers. In general, addition polymers with alpha substituted structures  
17 consistently exhibit lower ceiling temperatures than their unsubstituted parent species and are strong  
18 candidate materials. Polymers from the class of materials called condensation polymers, as well as  
19 the class of materials called photoresist polymers, may also have some utility, especially if they  
20 decompose to volatile materials. The spectrum of candidate materials is wide and many polymers



1 propellants can be used as the matrix material. Not all will be ideal in all characteristics. For  
2 example, repolymerization of a polymeric matrix material on the receiving substrate may be a  
3 problem with some materials. Other factors to be considered in the selection of the matrix material  
4 include the absorption of UV laser radiation, volatility of native propellant material, efficiency of  
5 the unzipping process, products of unzipping or decomposition and their volatility/toxicity, kinetic  
6 energy imparted by the propellant, degree of repolymerization, inertness of binder material, inertness  
7 of unzipped or decomposed propellant, cost, availability, purity, and processability with the material  
8 of interest to be deposited.

9 Specific polymeric matrix materials include, but are not limited to, the following: polyacrylic  
10 acid -butyl ester, nitrocellulose, poly(methacrylic acid)-methyl ester (PMMA), poly(methacrylic  
11 acid)-n butyl ester (PBMA), poly(methacrylic acid)-t butyl ester (PtBMA), polytetrafluoroethylene  
12 (PTFE), polyperfluoropropylene, poly N-vinyl carbazole, poly(methyl isopropenyl ketone), poly  
13 alphas-methyl styrene, polyacrylic acid, alpha phenyl-, methyl ester, polyvinylacetate,  
14 polyvinylacetate with zincbromide present, poly(oxymethylene), phenol-formaldehyde positive  
15 photoresist resins and photobleachable aromatic dyes.

16 The matrix material may also contain components that assist in the bonding of the transfer  
17 material to the receiving substrate or that assist in the bonding of particles of the transfer material  
18 to each other after they are deposited on the receiving substrate.

19 Examples of possible transfer material - matrix material combinations for the transfer of  
20 electronic materials include alumina (transfer material) with phosphoric acid (matrix material),

1 barium titanate (transfer material) with poly(methacrylic acid), n-butyl ester (PBMA) (matrix  
2 material), yttrium iron garnet (transfer material) with poly(methacrylic acid), n-butyl ester (PBMA)  
3 (matrix material), and nickel (transfer material) with KPR, (a phenol-formaldehyde positive  
4 photoresist polymer) (matrix material).

5 Examples of possible transfer material - matrix material combinations for the transfer of  
6 chemoselective polymers are SXFA (poly(oxy {methyl[4-hydroxy-4,4-bis(trifluoromethyl)but-1-en-  
7 1-yl] silylene})) (transfer material) with *t*-butanol (matrix material) and P4V (poly(4-  
8 vinylhexafluorocumyl alcohol)) (transfer material) with acetophenone (matrix material).

9 The transfer material and the matrix material may be combined to form the coating on the  
10 front surface of the laser transparent support in any manner that is sufficient to carry out the purpose  
11 of the invention. If the transfer material is soluble to some extent in the matrix material, the transfer  
12 material may be dissolved in the matrix material. Alternatively, if the transfer material is not soluble  
13 in a suitable solvent, the transfer material may be mixed with a matrix material to form a colloidal  
14 or particulate suspension or condensed phase. Still another alternative is to combine the matrix  
15 material and the transfer material with a solvent that volatilizes after the mixture is applied to the  
16 laser transparent support. The matrix material can also include soluble or insoluble dopants, that is,  
17 additional compounds or materials that one may wish to deposit onto the film.

18 The mixture of the transfer material and the matrix material may be applied to the front  
19 surface of the laser transparent support by any method known in the art for creating uniform coatings  
20 on a surface, including, for example, by spin coating, ink jet deposition, jet vapor deposition, spin

1 spray coating, aerosol spray deposition, electrophoretic deposition, pulsed laser deposition, matrix  
2 assisted pulsed laser evaporation, thermal evaporation, sol gel deposition, chemical vapor deposition,  
3 sedimentation and print screening. Typically, the mixture of the transfer material and the matrix  
4 material will be applied to the front surface of the laser transparent substrate to form a coating that  
5 is between about .1  $\mu\text{m}$  and about 100  $\mu\text{m}$  in thickness. Preferably, the coating is greater than about  
6 1  $\mu\text{m}$  in thickness, and, most preferably, is between about 1  $\mu\text{m}$  and about 20  $\mu\text{m}$  in thickness. The  
7 thicker the coating, the more of the transfer material can be transferred at one time, which is an  
8 advantage of the present invention over laser transfer methods that use thin films. On the other hand,  
9 a coating that is too thick will not desorb when exposed to the pulsed laser.

10 If the mixture of the transfer material and the matrix material is a liquid at room temperature,  
11 the mixture may be coated onto the front surface of the laser transparent support and then the mixture  
12 may be frozen to form a solid coating. The target substrate may be kept frozen while the coating is  
13 being exposed to a source of laser energy during the deposition process.

14 The laser transparent support is typically planar, having a front surface that is coated with  
15 the mixture of the transfer material and the matrix material and a back surface that can be positioned  
16 so that laser energy can be directed through the support. The composition of the laser transparent  
17 support is selected in accordance with the particular type of pulsed laser that is used. For example,  
18 if the laser is a UV laser, the laser transparent support may be a UV-transparent material including,  
19 but not limited to fused silica or sapphire. If the laser is an IR laser, the laser transparent support may  
20 be an IR-transparent material including, but not limited to plastic, silicon, fused silica, or sapphire.

1 Similarly, if the laser is a visible laser, the laser transparent support may be a material that is  
2 transparent in the visible range, including, but not limited to soda-lime and borosilicate glasses.

3 Any suitable source of laser energy may be used in the present invention. In general, a pulsed  
4 laser is preferred. (As used herein, the terms " pulsed laser" and "source of pulsed laser energy" are  
5 used interchangeably to refer to any device that creates a pulsed laser beam.) Lasers for use in  
6 accordance with the present invention can be any type such as are generally used with other types  
7 of laser deposition. Pulsed lasers are commercially available within the full spectral range from UV  
8 to IR. Typically, such lasers emit light having a wavelength in the range of about 157 nm - 1100 nm,  
9 an energy density of about 0.05 - 10 J/cm<sup>2</sup> (typically about 0.1 - 2.0 J/cm<sup>2</sup>), a pulsewidth of about  
10 10<sup>-12</sup> - 10<sup>-6</sup> second and a pulse repetition frequency of about 0 to greater than 20,000 Hz. In general,  
11 energy density (fluence) affects morphology; higher energies tend to produce deposited films that  
12 have larger particles. Examples of suitable lasers include, but are not limited to, pulsed gas lasers  
13 such as excimer lasers, i.e. F<sub>2</sub> (157 nm), ArF (193 nm), KrF (248 nm). XeCl (308 nm), XeF (351  
14 nm), CO<sub>2</sub>, nitrogen, metal vapor, etc., pulsed solid state lasers such as Nd:YAG, Ti:Sapphire, Ruby,  
15 diode pumped, semiconductor, etc., and pulsed dye laser systems. Typically, the particular laser is  
16 selected with regard to the absorption wavelengths of the matrix material.

17 The source of pulsed laser energy, the target substrate and the receiving substrate can be  
18 positioned with respect to each other and moved with respect to each other by any means known in  
19 the art for supporting a laser, target substrate and receiving substrate and moving them in a  
20 controlled and defined manner. For example, similar positioning means and moving means for a

1 laser, target and receiving substrate are known in the fields of laser transfer deposition and laser  
2 induced forward transfer. The laser may be positioned in any location that provides an optical path  
3 between itself and the target substrate so that sufficient laser energy can be directed to defined  
4 positions on the target substrate. The dimensions of the pulsed laser beam can be controlled by any  
5 means known in the art so that only a precisely defined area of the target substrate is exposed to the  
6 pulsed laser energy and so that only a precisely defined portion of the coating desorbs. The receiving  
7 substrate should be positioned so that when the coating on the target substrate is desorbed, the  
8 transfer material can be deposited at a defined location on the receiving substrate. Also, there should  
9 be enough space between the target substrate and the receiving substrate so that volatilized matrix  
10 material, or byproducts from laser-induced decomposition of the matrix material, can escape from  
11 the space between the target substrate and the receiving substrate. Preferably, the receiving substrate  
12 is positioned about 10 to about 100  $\mu\text{m}$  from the coating on the front surface of the target substrate.  
13 The laser, target substrate, and the receiving substrate should be moveable with respect to each other  
14 so that the transfer material can be deposited in a pattern and so that after the coating desorbs at one  
15 location on the target substrate, the pulsed laser energy can be directed to another location on the  
16 target substrate where the coating has not yet desorbed. For example, to deposit a line of material  
17 on the receiving substrate, the laser is moved with respect to the target substrate and the receiving  
18 substrate, which may be held stationary with respect to each other. As the laser moves with respect  
19 to the substrate, it directs laser energy to a new location on the target substrate where the coating has  
20 not yet desorbed, and causes the transfer material to be deposited onto a new location on the

1 receiving substrate. The successive locations may overlap to the extent necessary to create a  
2 continuous line of material on the receiving substrate. To increase the thickness of a deposit at a  
3 particular location, the laser and the receiving substrate are held stationary with respect to each other  
4 and the target substrate is moved with respect to the laser and the receiving substrate so that as the  
5 target substrate moves with respect to the laser, laser energy is directed to a new location on the  
6 target substrate where the coating has not yet desorbed and since the laser and the receiving substrate  
7 are not moved with respect to each other, the transfer material is deposited onto the same location  
8 on the receiving substrate in an increasingly thickened deposit. (As used herein, the terms "moving  
9 [a] with respect to [b]" or "moving [a] and [b] with respect to each other" mean that either [a] or [b]  
10 can be moved to effect a change in their relative position.)

11 The apparatus of the present invention can be adapted so that a plurality of different transfer  
12 materials can be deposited consecutively onto a receiving substrate. This may be done by providing  
13 a plurality of target substrates each having a different coating with a different transfer material and  
14 providing a way to consecutively move each target substrate into a position for depositing material  
15 from that target substrate onto the receiving substrate. Consecutive deposition of different transfer  
16 materials can also be accomplished by providing a target substrate that is subdivided into a plurality  
17 of different subregions that each have a different coating with a different transfer material and  
18 providing a way to select a particular subregion and deposit the transfer material from that subregion  
19 onto the receiving substrate.

20 The apparatus of the present invention can also be adapted so that an entire pattern of transfer

Sub  
48

material is deposited simultaneously on a patterned substrate

Having described the invention, the following examples are given to illustrate specific applications of the invention, including the best mode now known to perform the invention. These specific examples are not intended to limit the scope of the invention described in this application.

### EXAMPLES

#### Example 1: Deposition of Alumina ( $\text{Al}_2\text{O}_3$ )

The coating for the target substrate for the deposition of alumina was prepared by mixing 2 grams of alumina, in the form of random-shaped powders having an average particle size of  $0.3\ \mu\text{m}$ , with 1 ml of a matrix material, phosphoric acid, in 9 ml of methanol and then applying the solution to one side of a 5 cm diameter fused silica disc by spin coating to form an  $\text{Al}_2\text{O}_3/\text{H}_3\text{PO}_4$  coating about 1 to  $2\ \mu\text{m}$  thick. Using an excimer pulsed laser operating at 248 nm and at a fluence of  $300\ \text{mJ}/\text{cm}^2$ , focused through the fused silica disk to strike the coating in a  $25\ \mu\text{m}$  laser spot, it was possible to transfer the alumina powders from the silica disc to a receiving substrate surface located  $25\ \mu\text{m}$  away. Each laser shot produced a  $25\ \mu\text{m}$  disc-shaped deposit about  $1\ \mu\text{m}$  thick. To create a line of deposited BTO on the substrate, the laser was moved in a line relative to the substrate and the receiving substrate. To increase the thickness of the deposit at a particular location, the laser and the receiving substrate were held stationary to each other for several shots while the target substrate was moved. With this technique, a dielectric layer for a capacitor was formed.

**Example 2: Deposition of Barium Titanate ( $\text{BaTiO}_3$ , also referred to as "BTO")**

The coating for the target substrate for the deposition of barium titanate was prepared by mixing 1 gram of BTO, in the form of random-shaped powders having an average particle size of  $1\ \mu\text{m}$ , with 0.05 grams of a matrix material, poly(methacrylic acid), n-butyl ester (PBMA) in 10 ml of chloroform and then applying the solution to one side of a 5 cm diameter fused silica disc by spin coating to form a BTO/PBMA coating about 1 to 2  $\mu\text{m}$  thick. Using an excimer pulsed laser operating at 248 nm and at a fluence of  $400\ \text{mJ}/\text{cm}^2$ , focused through the fused silica disk to strike the coating in a  $25\ \mu\text{m}$  laser spot, it was possible to transfer the BTO powders from the silica disc to a receiving substrate surface located  $25\ \mu\text{m}$  away. Each laser shot produced a  $25\ \mu\text{m}$  disc-shaped deposit about  $1\ \mu\text{m}$  thick. To create a line of deposited BTO on the substrate, the laser was moved in a line relative to the substrate and the receiving substrate. To increase the thickness of the deposit at a particular location, the laser and the receiving substrate were held stationary to each other for several shots while the target substrate was moved. With this technique, a dielectric layer for a capacitor was formed.

**Example 3: Deposition of Yttrium Iron Garnet ( $\text{Y}_3\text{Fe}_5\text{O}_{12}$ , also referred to as "YIG")**

The coating for the target substrate for the deposition of yttrium iron garnet was prepared by mixing 1 gram of YIG, in the form of spherical powders having an average particle size of  $1\ \mu\text{m}$ , with 0.05 grams of a matrix material, poly(methacrylic acid), n-butyl ester (PBMA) in 10 ml of chloroform and then applying the solution to one side of a 5 cm diameter fused silica disc by spin coating to form a YIG/PBMA coating about 1 to 2  $\mu\text{m}$  thick. Using an excimer pulsed laser



1 operating at 248 nm and at a fluence of 400 mJ/cm<sup>2</sup>, focused through the fused silica disk to strike  
2 the coating in a 25 μm laser spot, it was possible to transfer the YIG powders from the silica disc  
3 to a receiving substrate surface located 25 μm away. Each laser shot produced a 25 μm disc-shaped  
4 deposit about 1 μm thick. To create a line of deposited BTO on the substrate, the laser was moved  
5 in a line relative to the substrate and the receiving substrate. To increase the thickness of the deposit  
6 at a particular location, the laser and the receiving substrate were held stationary to each other for  
7 several shots while the target substrate was moved. With this technique, a ferrite core for an inductor  
8 was formed.

#### 9 **Example 4: Deposition of Nickel**

10 The coating for the target substrate for the deposition of nickel was prepared by mixing 2  
11 grams of nickel, in the form of spherical powders having an average particle size of 1 μm, with 10  
12 ml of a matrix material, diazonaphthoquinone-novolac (a phenol-formaldehyde positive photoresist  
13 polymer sold by Kodak under the tradename "KPR") and then applying the solution to one side of  
14 a 5 cm diameter fused silica disc by spin coating to form a nickel/KPR coating about 1 to 2 μm  
15 thick. Using an excimer pulsed laser operating at 248 nm and at a fluence of 450 mJ/cm<sup>2</sup>, focused  
16 through the fused silica disk to strike the coating in a 40 μm laser spot, it was possible to transfer  
17 the YIG powders from the silica disc to a receiving substrate surface located 25 μm away. Each laser  
18 shot produced a 40 μm disc-shaped deposit about 0.3 μm thick. To create a line of deposited nickel  
19 on the substrate, the laser was moved in a line relative to the substrate and the receiving substrate.  
20 To increase the thickness of the deposit at a particular location, the laser and the receiving substrate

Docket No.: N.C. 79,702

PATENT APPLICATION

Inventor's Name: Douglas B. Chrisey, R. Andrew McGill and Alberto Pique

1 were held stationary to each other for several shots while the target substrate was moved. With this  
2 technique, various lines of deposited nickel were formed.

3 Obviously, many modifications and variations of the present invention are possible in light  
4 of the above teachings. It is therefore to be understood that, within the scope of the appended claims,  
5 the invention may be practiced otherwise than as specifically described.

000000-000000